UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
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OFFICE OF
RESEARCH AND DEVELOPMENT

November 27, 2018

Ken Kloo, Director
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Subject: NJ DEP Report #2: Non-targeted Analysis of (ClPFPECA) in Soil and Vegetation Samples

Dear Mr. Kloo:

I am pleased to provide you with the laboratory report of non-targeted analysis results for Chloro Perfluoro Polyether Carboxylate (ClPFPECA) concentrations in soils and vegetation. This is the second in a series of reports prepared as a part of EPA Office of Research and Development's (ORD) collaboration with the New Jersey Department of Environmental Protection (NJ DEP) and EPA Region 2 on the study, "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." This report includes concentration results for PFAs in 24 soil and 24 vegetation samples. The ORD Principal Investigators (PIs) for this study are Drs. Andy Lindstrom, Mark Strynar, and John Washington. The results in this report were generated by Dr. John Washington in our Athens, Georgia laboratory. It is my understanding that these samples were collected by NJ DEP between November 8 to 10, 2017 from various locations in the vicinity of the Solvay and Dupont facilities.

We do not interpret exposure or risk from the values presented in this report. EPA does not currently have health-based standards, toxicity factors, or associated risk levels for per- or poly-fluorinated alkyl substances (PFAS), other than perfluorooctanoic acid (PFOA), perfluorocatane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided indicate the presence of certain PFAs in soil samples, it does not offer interpretation as to human or environmental exposure or risk.

Thank you for providing us with this opportunity for collaboration that helps to further both EPA's and New Jersey's understanding of an important public health issue. If you have any questions or concerns about this report, do not hesitate to contact me at (919) 541-2107 or via email at watkins.tim@epa.gov or Tim Buckley at (919) 541-2454 or via email at buckley.timothy@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H. Watkins
Director
National Exposure Research Laboratory
Office of Research and Development

Enclosure

CC:

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ORD Technical Report # NJ-2: ORD Technical Support to New Jersey DEP - Non-targeted PFAS Measurements in Soil and Vegetation Samples

This report supports a collaborative study with EPA ORD, Region 2, and NJ DEP entitled "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." NJ DEP assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis of PFAS. ORD's analysis and support team for this data report are listed in Table 1.

Table 1. EPA Office of Research and Development analysis and report team.

Responsibility	Personnel
ORD Principal Investigators	Andy Lindstrom, Mark Strynar, John Washington
Laboratory chemistry	John Washington (PI), Tom Jenkins
Quality Assurance Review	Brittany Stuart
Management coordination and review	Brian Schumacher, Tim Buckley
Report Preparation	Kate Sullivan, Tim Buckley

[1]

This 2nd report includes results of non-targeted analysis of 24 soil samples and 24 vegetation samples collected by NJ DEP from Nov 8 to Nov 10, 2017. Samples were sent to and analyzed for PFAS compounds under the direction of Dr. John Washington at ORD's laboratory in Athens, GA. Samples were received on November 14, 2017.

Methods in Brief

The PFAS reported here were extracted and analyzed according to methods documented within an approved Quality Assurance Project Plan (QAPP)[1]. PFAS was identified and quantified using a non-targeted analysis approach. The non-targeted analysis differs from targeted analysis in that chemical identification and quantification does not have the benefit of being based on a known standard for each compound. Accordingly, there is more uncertainty both in terms of identification and concentration estimation for these non-targeted analytes.

Each sample was divided into three ~lg aliquots and extracted individually. Samples were extracted with 90%/10% acetonitrile water followed by a liquid/liquid cleanup. Samples were first analyzed by liquid chromatography/mass spectrometry using a Waters Acquity UPLC coupled to a Waters Xevo quadrupole time-of-flight (QToF) mass spectrometer to identify the previously unknown PFAS. The non-targeted PFAS were identified based on a combination of high-resolution mass spectral data along with patterns of fragmentation. This was followed by analysis on a Waters Acquity UPLC coupled to a Waters Quattro Premier tandem mass

[1] [1]National Exposure Research Laboratory, Quality Assurance Project Plan: Detection, Evaluation and Assignment of Multiple Poly and Per-fluoroalkyl Substances (PFAS) in environmental media from an industrialized area of New Jersey. Prepared for New Jersey Department of Environmental Protection (NJ DEP), September 14, 2017.

spectrometer providing semi-quantitation. PFAS concentrations were estimated using $^{13}C_5$-labeled perfluorononanoic acid (M5PFNA) as a matrix internal standard by simple peak-area ratio.

The quantification of the non-targeted analyte assumes that the mass spectrometer responds to M5PFNA as it does the reported analytes, i.e. yielding identical chromatographic peak areas for a given concentration. Our experience with PFAS suggests that this means of estimation is within an order of magnitude of the actual concentration. Even though the absolute concentration estimate will be uncertain, relative comparisons between samples for a given congener will be much less so.

Results

Quality control parameters and results are provided in Appendix A. Our QC evaluations are based on measures of precision from duplicate analysis of both samples and extracts. It was not possible to evaluate accuracy or recovery without the benefit of standards. We do not have results from field duplicate soil and vegetation samples at this time.

Based on QC tests and experience, the laboratory PI identified a threshold for reliably reproducible analysis at peak area >100. This value is considered the Level of Quantitation (LOQ) for non-targeted analysis of soil and vegetation samples. Using this method, the LOQ concentration varies by analyte. The concentrations of samples with peak area less than the LOQ are considered estimates and are flagged accordingly.

Analytical and sample precision was generally good for analytes with peak area greater than LOQ and met QAPP specifications for precision

We tentatively identified the presence of 9 novel PFAS in soil and plant samples. The nine PFAS are congeners of chloroperfluoro polyether carboxylate (ClPFPECA). Their generic structure is shown in Figure 1 and their mass spectral features are provided in Table 2. Based on the prevalence of these congeners associated with Solvay, we have high confidence in these chemical identifications. This identification is also consistent with measurements by Wang et al. 2018.[2]

[2] Wang Y, Yu N, Zhu X, Guo H, Jiang J, Wang X, Shi W, Wu J, Yu H, Wei S. Suspect and Nontarget Screening of Per- and Polyfluoroalkyl Substances in Wastewater from a Fluorochemical Manufacturing Park. Environ Sci Technol. 2018 Oct 2;52(19):11007-11016. doi: 10.1021/acs.est.8b03030. Epub 2018 Sep 24. PubMed PMID: 30211545.

Figure 1. Generic Structure of Chloro Perfluoro Polyether Carboxylate (ClPFPECA). There are nine congeners with m and n varying from 0-3.

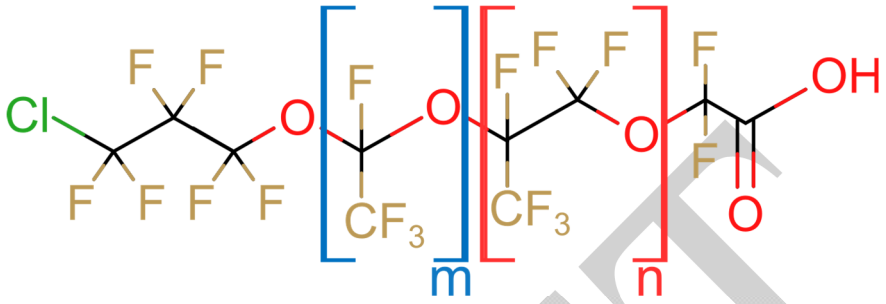

Table 2. MS/MS Features of Chloro-perfluoro-polyether (ClPFPECA) Congeners Identified in Soils and Plants Using Non-Targeted Analysis that are the Subject of this Report.

Carbon Chain Length	Anion Formula	Number of Ethyl, Propyl Groups	Molecular Mass (g/mol)	Precursor	Fragment	Elution Time (m) Soils (Plants)
7	$C_7ClF_{12}O_4$	**1,0**	410.9294	316.9447	200.9542	2.3 (2.3)
8	$C_8ClF_{14}O_4$	**0,1**	460.9262	366.9395	200.9542	2.6 (2.6)
9	$C_9ClF_{16}O_5$	**2,0**	526.9179	432.9312	200.9542	3.4 (3.4)
10	$C_{10}ClF_{18}O_5$	**1,1**	576.9147	482.9280	200.9542	3.9 (3.9)
11	$C_{11}ClF_{20}O_5$	**0,2**	626.9115	532.9249	200.9542	4.6 (4.23)
11	$C_{11}ClF_{20}O_6$	**3,0**	642.9064	548.9198	200.9542	4.9 (4.47)
12	$C_{12}ClF_{22}O_6$	**2,1**	692.9032	598.9166	200.9542	5.5 (5.25)
13	$C_{13}ClF_{24}O_6$	**1,2**	742.9000	648.9134	200.9542	6.1 (6.1)
14	$C_{14}ClF_{26}O_6$	**0,3**	792.8968	698.9102	532.9249	6.7 (6.4)

The estimated concentrations of PFAS congeners listed in Table 2 are given by sample IDs assigned by NJ DEP for 24 soil samples in Table 3. Please note that analysis of 5 soil core samples has not yet been completed. Estimated concentrations of the same congeners for 24 plant samples are presented in Table 4.

Summary of observations for soil:

- 9 PFAS congeners were found at measurable concentrations in at least one soil sample with 3 congeners detected in all 24 of the samples (C8, C10, C11).
- Soil concentrations of C8, C10, and C11 were relatively high in most samples. The maximum PFAS concentration in soil was 1,580 pg/g for C10 at site PFSS008.
- Congeners C7, and C13 and C14 were either not detected or found at low concentrations at most sites.

Summary of observations for vegetation:

- 9 PFAS congeners were found at measurable concentrations in at least one of the vegetation samples, with 3 congeners detected in measurable concentrations in most of the vegetation samples (C8, C10, C11).
- Vegetation concentrations of C8, C10, and C11 were relatively high in most samples. The maximum PFAS concentration in vegetation was 9,750 pg/g for C10 at site PFSS008.
- Congeners C7, C9, and C11 to C14 were either not detected or found at low concentrations in most of the vegetation samples.
- C8, C10 and C11 congeners were found in relatively high concentrations in both soil and vegetation at most sites. Concentrations were consistently greater in vegetation than soils, with a maximum ratio $\frac{Veg}{Soil}$ for C8 of 40.7 observed at site PFSS008.

Table 3. Semi-Quantitative Concentrations of PFAS Congeners in Soil Samples Determined with Non-targeted Analysis Expressed in pg/g.

Carbon Length	*C7*	*C8*	*C9*	*C10*	*C11*	*C11*	*C12*	*C13*	*C14*
Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{14}ClF_{26}O_6$
Ethyl, Propyl Groups	**1,0**	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**0,3**
Soil Sample ID	**Soil Concentrations as M5PFNA (by simple ratios to matrix internal standard in pg/g soil)**								
PFSS001	2.9 (U)	703	13.9	1350	509	35.4	108	9.1	31.5
PFSS002	ND	63.5	1.4 (U)	154	57.4	3.7	11.8	1.4 (U)	3.9
PFSS003	ND	61.2	1.3 (U)	85.7	42.3	3.9	15.7	0.8 (U)	2.0 (U)
PFSS004	13.9	293	3.9	330	89.0	5.4	12.3	1.3 (U)	2.3 (U)
PFSS005	0.5 (U)	95.2	0.7 (U)	72.5	22.5	1.5 (U)	2.6 (U)	0.1 (U)	0.4 (U)
PFSS006	ND	68.5	1.1 (U)	87.7	29.1	0.8 (U)	4.4	ND	ND
PFSS007	0.5 (U)	75.8	0.7 (U)	31.7	8.4	0.7 (U)	1.1 (U)	ND	0.1 (U)
PFSS008	0.7 (U)	356	8.8 (U)	1580	600	44.8	125	11.0	31.9
PFSS009	0.6 (U)	89.5	1.1 (U)	68.4	33.7	2.1 (U)	5.7	0.2 (U)	1.3 (U)
PFSS010	ND	29.4	ND	34.7	18.2	0.8 (U)	4.3	ND	1.2 (U)
PFSS011	0.3 (U)	75.9	1.0 (U)	68.8	20.7	1.8 (U)	1.7 (U)	ND	0.3 (U)
PFSS012	ND	79.8	1.4 (U)	84.7	32.1	2.0 (U)	8.8	ND	ND
PFSS013	ND	45.0	ND	25.1	10.1	1.2 (U)	4.2	ND	0.3 (U)
PFSS014	ND	68.7	2.4 (U)	92.1	42.9	1.7 (U)	7.1	0.6 (U)	0.8 (U)
PFSS015	1.2 (U)	74.3	1.4 (U)	91.5	26.1	1.3 (U)	3.4 (U)	ND	1.3 (U)
PFSS016	ND	33.3	0.9 (U)	12.1	2.7	ND	ND	ND	ND
PFSS017	ND	23.1	ND	15.3	9.2	ND	3.2 (U)	ND	ND
PFSS018	ND	14.5	0.3 (U)	19.1	8.4	ND	0.9 (U)	0.3 (U)	ND
PFSS019	ND	113	1.0 (U)	56.2	16.6	0.9 (U)	2.8 (U)	ND	0.3 (U)
PFSS020	ND	66.9	ND	76.3	28.1	1.4 (U)	5.4	ND	1.5 (U)
PFSS021	ND	33.4	ND	33.4	11.5	ND	2.9 (U)	ND	0.4 (U)
PFSS022	ND	14.4	ND	10.1	4.6 (U)	ND	0.7 (U)	ND	ND
PFSS023	ND	83.6	1.7 (U)	99.5	24.0	ND	5.4	ND	1.1 (U)
PFSS024	ND	32.3	0.8 (U)	21.5	10.5	ND	3.2 (U)	ND	ND

ND: Sample result is less than the limit of detection (<LOD), no peak observed.

U: Peak observed but less than the limit of quantitation (<LOQ). The associated sample value is an estimate.

Table 4. Estimated Relative Concentrations of PFAS Congeners in Vegetation Samples Determined with Non-targeted Analysis Expressed in pg/g.

Carbon Length	*C7*	*C8*	*C9*	*C10*	*C11*	*C11*	*C12*	*C13*	*C14*
Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{14}ClF_{26}O_6$
Ethyl, Propyl Groups	**1,0**	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**0,3**
Vegetation Sample ID	**Vegetation Concentrations as M5PFNA (by simple ratios to matrix internal standard in pg/g dry plant)**								
PFVG001	ND	1,680	ND	856	371	15.8	49.3	ND	10.3 (U)
PFVG002	ND	269	ND	128	82.4	ND	10.6 (U)	ND	ND
PFVG003	ND	289	ND	475	344	30.8	89.5	ND	5.9 (U)
PFVG004	ND	1,010	80.1 (U)	401	126	ND	ND	ND	ND
PFVG005	ND	1,880	ND	579	152	ND	ND	ND	ND
PFVG006	ND	334	ND	126	21.8	ND	ND	ND	ND
PFVG007	ND	116	ND	119	53.9	ND	ND	ND	ND
PFVG008	ND	14,500	80.0	9,750	3,100	222	387	30.0	87.2
PFVG009	ND	266	74.0 (U)	1,010	173	ND	42.4	ND	ND
PFVG010	ND	149	ND	259	44.7	ND	7.6 (U)	ND	ND
PFVG011	ND	261	ND	953	339	ND	ND	ND	ND
PFVG012	ND	161	ND	56.9	7.2 (U)	ND	ND	ND	ND
PFVG013	ND	470	ND	48.5	9.2 (U)	ND	ND	ND	ND
PFVG014	ND	945	ND	181	26.9	ND	119 (U)	ND	2.1 (U)
PFVG015	ND	769	ND	452	60.5	ND	26.3	ND	2.0 (U)
PFVG016	ND	289	ND	44.1	9.0 (U)	ND	4.2 (U)	ND	ND
PFVG017	ND	150	ND	36.5	7.1 (U)	ND	6.4 (U)	ND	ND
PFVG018	ND	423	ND	ND	ND	ND	ND	ND	ND
PFVG019	ND	3,230	ND	381	51.7	ND	ND	ND	ND
PFVG020	ND	336	ND	325	49.2	7.1 (U)	14.8 (U)	ND	ND
PFVG021	4.1 (U)	33.6	ND	23.5	10.9 (U)	ND	ND	ND	ND
PFVG022	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFVG023	ND	644	ND	304	73.5	ND	23.5	ND	ND
PFVG024	31.4	970	ND	32.8	7.9 (U)	ND	ND	ND	ND

ND: Sample result is less than the limit of detection (<LOD), no peak observed.

U: Peak observed but less than the limit of quantitation (<LOQ). The associated value is an estimate.

Appendix A

Quality Assurance Documentation

The quality assurance and control analyses described in this Appendix A refer to 24 soil samples (labeled PFSS) and 24 vegetation samples (labeled PFVG) received at ORD's Athens Georgia laboratory on November 14, 2017. The soil samples also included 2 field duplicates and 2 field blanks. There were no QC samples associated with vegetation samples. Soil core samples labeled PFSC (n=4 plus one duplicate) were also received November 14, 2017. Analysis of soil core samples has not been completed.

Each sample was divided into three ~lg aliquots and extracted individually. Non-targeted analysis results presented in Tables 3 and 4 were based on measurement of one 1 aliquot. Quality control assessment was limited to evaluation of precision determined by repeated measurement of the same aliquot (referred to in laboratory files as 1st rep). Sample precision was determined by comparison of values measured from two different aliquots from the same sample (referred to in laboratory files as 2nd rep). Analysis of the SS series field QC samples (duplicates and blanks) has not been completed.

The ORD PI identified a threshold for reliable reproducible analysis at peak area >100 based on experience with the analysis and supported by the QC analysis of the analytical replicates described here. Non-detection was determined as peak area of 0. Peak area > 100 defines the threshold of reliable reproducibility, taken as the Limit of Quantitation (LOQ) for the non-targeted analysis. Not that basing the LOQ on peak area results in different LOQ concentrations by analyte. Sample results are flagged according to peak area status in Tables 3 and 4.

The precision goal for analytical and sample accuracy was 50% for the Relative Percent Difference of the two samples calculated as:

$$\text{Relative \% Difference (RPD)} = (\text{ABS}\left[\frac{Sample\ 1 - Sample\ 2}{(Sample\ 1 + Sample 2)/2}\right]) * 100$$

The Quality Control results for repeated measures are summarized for soils in Table A1 and for plants in Table A2. Samples greater than LOQ generally met QAPP goals. Soil and vegetation samples with peak areas ND < Value < LOQ were far more variable in precision evaluations summarized below.

Soil samples. The analyte concentrations in soil samples greater than LOQ had very good repeatability. All analytical (1st rep) comparisons of sample/analyte were within 30% of the first sample (Mean RPD). Mean RPD was 8% for 34 valid comparisons where both samples were greater than ND. Mean RPD for precision of sample precision (2nd rep) for soils < LOQ was 16.2% while 3 of 34 comparisons exceeded 30%.

Analytical precision (1st rep) was not as good for analytes ND < Value < LOQ. Mean RPD for this group was 34.9% of 16 valid comparisons with 7 exceeding 30%. Sample precision (2nd rep) mean RPD was 31.9% with 6 of 12 comparisons exceeding 30%.

Vegetation samples. Precision results for vegetation samples was more variable than soils. Analytical precision of samples > LOQ had mean RPD of 18% with 6 of 26 valid comparisons exceeding 30%. Mean RPD for sample precision (2nd rep) was 36% with 16 of 26 comparisons exceeding 30%. Mean RPD of both analytical (4) and sample (3) precision of samples < LOQ averaged 100%

Table A1. Summary of quality control assessment for non-targeted analysis of soils.

Quality Assurance Measure	Quality Control Measure	Quality Objective	Result	Corrective Action
Method Sensitivity	**Limit of Detection (LOD)**	None specified	LOD is defined as the point at which the instrument detects an analytical peak	Non-detected peak areas are reported as "ND"
	Limit of quantitation (LOQ) Limit of reliable reproducibility	None specified	LOQ is defined at 100 peak area counts based on Analyst interpretation and analytical accuracy Peak area <100 is <LOQ and peak >100 is >LOQ	Results <LOQ flagged with "U"
Analytical Accuracy	Analytical Precision for samples > LOQ (n=34)	RPD% ± 30%	Mean RPD 8.0% + 6.5% (SD) (Ranging from 0 to 24%)	Results exceeding criteria are flagged with "JP"
	Analytical Precision for samples LOD < Sample < LOQ n= 16	RPD% ± 50%	Mean RPD 34.9% + 32.4% (SD) (Ranging from 1 to 112%)	Results exceeding criteria are flagged with "JP"
Sample Accuracy	Sample Precision for samples > LOQ (n=36)	RPD% ± 50%	Mean RPD 16.2% + 11.1% (SD) (Ranging from 1 to 33%)	None necessary
	Sample Precision for samples with LOD < Sample < LOQ N=12	RPD% ± 30%	Mean RPD 31.9% + 24.4% (SD) (Ranging from 0 to 66%)	None necessary
	Field duplicates (n=2)	RPD% ± 50%	Analysis not yet completed	None necessary
Bias	Instrument blanks (i.e. process blanks)	<LOD	All process blanks (n=6) were free of reported analytes.	None necessary
	Field blanks (n=2)	None specified	Analysis not yet completed	None necessary

Table A2. Summary of quality control assessment for non-targeted analysis of vegetation samples.

Quality Assurance Measure	Quality Control Measure	Quality Objective	Result	Corrective Action
Method Sensitivity	**Limit of Detection (LOD)**	None specified	LOD is defined as the point at which the instrument detects an analytical peak	Non-detected peak areas are reported as "ND"
	Limit of quantitation (LOQ) Limit of reliable reproducibility	None specified	LOQ is defined at 100 peak area counts based on Analyst interpretation and analytical accuracy Peak area <100 is <LOQ and peak >100 is >LOQ	Results <LOQ flagged with "U"
Analytical Accuracy	Analytical Precision for samples > LOQ (n=26)	RPD% ± 50%	Mean RPD 17.9% + 14.0% (SD) (Ranging from 0 to 54%)	Results exceeding criteria are flagged with "JP"
	Analytical Precision for samples with LOD < Sample < LOQ n= 4	RPD% ± 50%	Mean RPD 100% + 89.1% (SD) (Ranging from 1 to 184%)	Results exceeding criteria are flagged with "JP"
Sample Accuracy	Sample Precision for samples > LOQ (n=26)	RPD% ± 50%	Mean RPD 36.4% + 27.4% (SD) (Ranging from 5 to 131%)	None necessary
	Sample Precision for samples with LOD < Sample < LOQ N=3	RPD% ± 50%	Mean RPD 95.4% + 67.2% (SD) (Ranging from 34 to 167%)	None necessary
Bias	Instrument blanks (i.e. process blanks)	<LOD	All process blanks (n=6) were free of reported analytes.	None necessary